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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with standard method procedures for determining the Chemical Oxygen Demand (COD) of a wastewater sample. Included are objectives, instructor guides, student handouts, and transparency masters. This module considers analytical procedures, preparation of reagents and interpretation of results. (Author/RH)

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CHEMICAL OXYGEN DEMAND

Training Module 5.107.2.77

Prepared for the

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September, 1977

SE 024 150

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Module No:	Module Title: Chemical Oxygen Demand
	Submodule Title:
Approx. Time: 5 hours	Topic: Introduction to COD COD Analysis Relationship of COD to BOD

Objectives:

Upon completion of this module the participant should be able to determine the COD of a sample given proper apparatus and reagents.

Instructional Aids:

Lab apparatus and reagents
Handouts
Overheads

Instructional Approach:

Lecture
Laboratory
Discussion

References:

EPA Methods for Chemical Analysis of Water & Wastewater
Standard Methods, 14th Ed.
Sawyer & McCarthy, Chemistry for Sanitary Engineers
EPA Effluent Monitoring Procedures: Nutrients

Class Assignments:

Complete a COD analysis

Instructor Notes

The EPA as a set of 35 mm slides showing COD analysis. This may be used optionally in the Introduction.

An optional procedure handout may be found in the EPA effluent monitoring procedures: Nutrient. This low level COD procedure is the same as the one in the module but written in a different format.

Lab apparatus and reagents should be supplied so that participants may work in groups of two or three.

Overheads are included for content value only the actual overhead should be made with colored 1/4 inch dry transfer letters.

Module No:	Module Title: COD
	Submodule Title:
Approx. Time: 1 hour	Topic: Introduction to COD

Objectives:

Upon completion of this topic the participant should be able to:

1. Indicate what is measured in the COD test.
2. Indicate how the COD test relates to the BOD and COD tests.
3. Indicate when the low range COD test should be used.
4. Indicate sampling procedures and sample preservation procedures for the COD test.

Instructional Aids:

Overheads

Instructional Approach:

Lecture
Discussion

References:

Methods for Chemical Analysis of waters and wastes
Standard Methods, 14th Ed.
Sawyer & McCarthy, Chemistry for Sanitary Engineers

Class Assignments:

None

Module No: _	Topic: Introduction to COD

Instructor Notes:	Instructor Outline:
Overhead Flow sheet Page 11	1. a. Discuss the COD test it terms of a measurement of oxygen required for oxidation to CO_2 and H_2O. b. Explain that COD test uses a potassium dichromate in a strongly acidic solution at an elevated temperature as the oxidizing material. c. Indicate that the amount of dicromate is measured after the test to determine how much was used in the test. A known amount is added before the test. d. Explain that a reflux condenser must be used to prevent the loss of volatiles. e. Explain that for some materials such as low-molecular-weight fatty acids are not oxidized unless there is a silver catalyst present. f. Indicate that aromatic hydrocarbons and pyridine are not oxidized under any circumstances. 2. a. Indicate that COD values are greater than BOD values for the same waste, because the COD test can oxidize biologically resistant organic matter such as lignin not oxidized in the BOD test wood-pulping wastes have high lignin values. b. Indicate that the COD test cannot differentiate between biologically oxidizable and biologically inert organic matter. c. Indicate that COD and BOD have a good correlation value given a consistant waste composition such as an industrial waste.

Module No:	Topic: Introduction to COD

Instructor Notes:	Instructor Outline:
Overhead Page 8 Low level High level COD Test	3. Explain that the oxydent, potassium dichromate is used at one concentration for samples of COD less than 50 and at a more concentrated level for COD greater than 50 mg/l. 4. a. Discuss and if possible demonstrate sampling procedures. b. Discuss and demonstrate proper sample preservation procedures. H_2SO_4 to pH 2, Cool to 4^0 C

CHEMICAL OXYGEN DEMAND TEST

LOW RANGE - - - - - - - - - - - - - - - - 10 TO 50 MG/L

HIGH RANGE - - - - - - - - - - - - - - - 40 TO 100,000 MG/L

Module No:	Module Title: COD
	Submodule Title:
Approx. Time: 3½ hours	Topic: COD Analysis

Objectives:

Upon completion of this topic the participant should be able to:

1. Identify the proper apparatus and reagents needed for the COD test.
2. Properly prepare reagents and glassware for the COD test.
3. Conduct the COD test given sample, reagents apparatus and procedures sheet.
4. Translate the raw data from the COD test into proper units of expression.

Instructional Aids:

Lab apparatus and reagents per high level handout
Handouts
Overheads

Instructional Approach:

Lab

References:

Standard Methods, 14th Ed.
EPA Methods Manual
EPA Effluent Monitoring Procedures: Nutrients

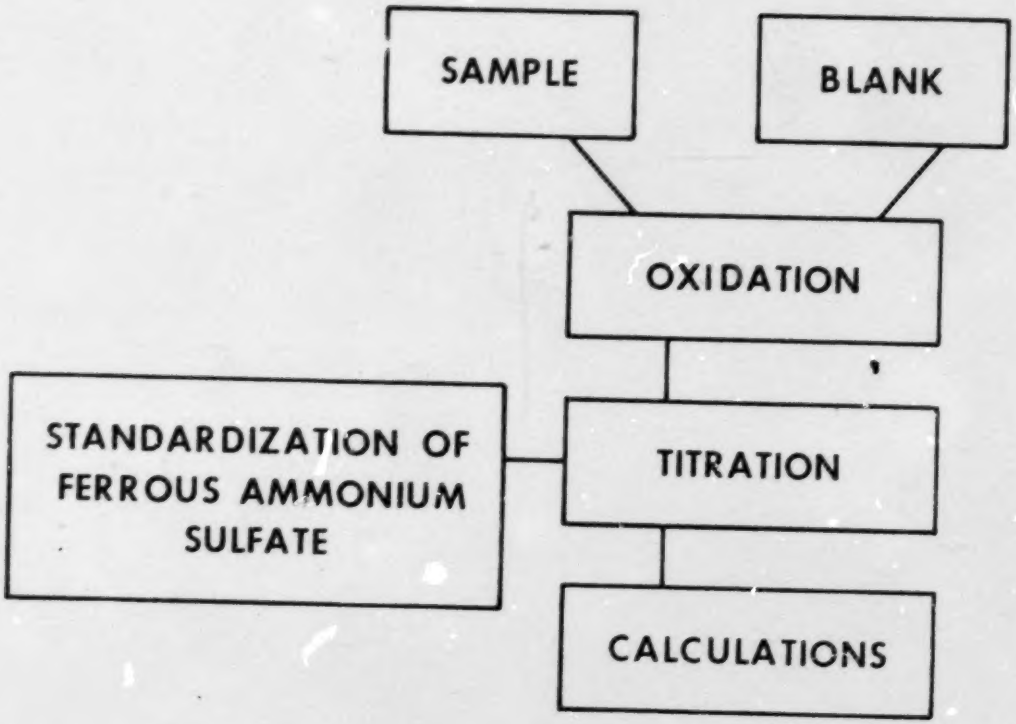
Class Assignments:

Conduct a COD analysis

Module No:	Topic: COD Analysis

Instructor Notes:	Instructor Outline:
	1. a. List and identify the proper apparatus and reagents needef rot the COD test.
	2. a. Demonstrate the makeup of reagents.
	b. Have groups of participants make up required reagents.
Handout Pages 12 - 21 COD procedure High range	3. a. Demonstrate the startup and end of the COD test.
	b. Discuss sample dilution and the green color of reduced dicromate.
	c. Demonstrate standardization procedures.
	d. Have participants conduct a COD high level test and standardize reagents.
Handout Bench sheet Page 22	4. a. Work sample calculations
	b. Have participants translate raw data from the test into proper units of expression.

FLOW SHEET:


SAMPLE
BLANK
OXIDATION
STANDARDIZATION OF FERROUS AMMONIUM SULFATE
TITRATION
CALCULATIONS

CHEMICAL OXYGEN DEMAND (COD)

Introduction

The chemical oxygen demand (COD) is an important test which measures the organic strength of wastewater. It measures those organic materials which can be oxidized by a strong chemical oxidizing agent, in this case potassium dichromate. The units of measurement of COD are in terms of the mg/l of oxygen involved in the oxidation reaction.

The COD measures some organic materials that bacteria are unable to utilize in the 5-day BOD test. In addition, waste which is too toxic for bacterial oxidation can be measured. For these reasons, the BOD values are normally 50 - 70% of the COD. In addition, the COD test has the advantage of requiring only about three hours compared to five days for the BOD,

In the test, the sewage sample is mixed with mercuric sulfate, sulfuric acid-silver sulfate reagent and the potassium dichromate oxidizing agent. The mixture is then refluxed (boiled and recondensed) for two hours to insure maximum oxidation. Since a known amount of chemical oxygen in the form of potassium dichromate ($K_2CR_2O_7$) is added to the mixture, the amount of oxygen used can be determined by measuring the amount of potassium dichromate remaining after the reflux period. This is accomplished by titrating the potassium dichromate with standardized ferrous ammonium sulfate. The COD is then expressed as mg/l or ppm.

The mercuric sulfate is added to the reflux to prevent interference from chlorides. The silver sulfate is added as a catalyst to aid in the oxidation of some organic alcohols and acids. Acid conditions necessary for the oxidation are maintained by the sulfuric acid.

Equipment

Reflux apparatus w/Friedrichs style condenser.

250-ml Erlenmeyer flask with ground glass neck, size 24/40.

Hot plate with 1,300 watt rating.

500-ml wide mouth Erlenmeyer flask.

Buret and Buret stand.

10 and 20-ml volumetric pipettes.

2 50-ml graduated cylinders.

Glass beads

Reagents

1. Standard Potassium Dichromate ($K_2Cr_2O_7$) 0.25 N

Dissolve 12.259 g dried $K_2Cr_2O_7$ in distilled water and dilute to one liter with distilled water. $K_2CR_2O_7$ must be previously dried at 103° C. for two (2) hours.

2. Sulfuric Acid (H_2SO_4) - Silver Sulfate (Ag_2SO_4) Reagent

Add 22 g of Ag_2SO_4 to a 9 lb. bottle of concentrated H_2SO_4. It may take one to two days for the Ag_2SO_4 to dissolve.

3. Standard Ferrous Ammonium Sulfate $(Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O)$ solution 0.25 N

Dissolve 98 g $(Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O)$ in distilled water, add 20 ml concentrated H_2SO_4, cool and dilute to one liter with distilled water. This solution is unstable and must be standardized with each set of tests.

4. Ferroin Indicator

Dissolve 1.485 g 1, 10 phenathroline ($C_{12}H_8N_2 \cdot H_2O$) and 0.695 g Iron (II) sulfate crystals ($FeSO_4 \cdot 7H_2O$) in distilled water and dilute to 100 ml with distilled water.

5. Mercuric Sulfate ($HgSO_4$)

Analytical grade crystals.

Procedure

1. Standardize Ferrous Ammonium Sulfate (FAS) Solution

While the samples and blank are refluxing (Step #8 below) standardize the FAS solution as follows:

a. Dilute 10.0 ml standard potassium dichromate to about 100 ml with distilled water. Use a volumetric pipette to measure the 10.0 ml.

b. Add 30 ml concentrated H_2SO_4 and cool.

c. Add 2 - 3 drops ferroin indicator.

d. Titrate with the ferrous ammonium sulfate in the buret. The color changes from orange to blue-green to reddish-brown. The end-point is the sharp change from blue-green to reddish-brown, although the blue-green may reappear on standing.

e. Calculate normality of FAS.

$$\text{Normality, FAS} = \frac{(\text{ml. } {}_2K_2Cr_2O_7) \times \text{Normality, } (K_2Cr_2O_7)}{\text{ml. FAS}}$$

$$= \frac{(10 \text{ ml}) \times (0.25 \text{ N})}{\text{ml. FAS}}$$

$$= \frac{2.5}{\text{ml. FAS}}$$

2. Place 0.4 g $HgSO_4$ in each 250 erlenmeyer flask

Duplicates should be run for each example.

3. Add 20.0 ml Sample

Or duluted sample to the reflux flask. Be sure sample is well mixed. If large particles exist, sample should be homogenized. Use volumetric pipette for this transfer.

4. Add 10.0 ml Standard $K_2Cr_2O_7$

   To the reflux flask. Use volumetric pipette.

5. Add 30 ml Sulfuric Acid - Silver Sulfate Reagent

   To the reflux flask. Use caution. Add a little at a time with constant mixing.

6. Prepare Reagent Blank

   Repeat steps 2 - 5 above except use distilled water in place of the 20.0 ml of sample.

7. Add Glass Boiling Beads

   About 15 - 20 beads to each reflux flask.

8. Reflux Samples and Blank

   Make sure contents are thoroughly mixed before proceeding to heating step. If this is not done, local hot spots may cause the flask to explode.

   Reflux for two hours.

   If the mixture turns completely green, the sample is too strong. Dilute the sample further and repeat the procedure.

9. Wash Condenser and Dilute

   After allowing the mixture to cool, wash down the condenser with about 25 ml distilled water. Transfer flask contents to a 500-ml wide mouth Erlenmeyer flask, washing out the reflux flask 4 or 5 times with distilled water. Do not discard boiling beads. Dilute to about 140 ml with distilled water. Cool again to room temperature.

10. Add 2 - 3 Drops Ferroin Indicator

11. Titrate With FAS

Titrate to the reddish-brown end-point as in the standardization of FAS. Remember to record initial and final buret readings when carrying out titrations.

Calculations

Calculate ml of FAS used by subtracting initial from final buret readings:

a = ml FAS used to titrate blank

b = ml FAS used to titrate sample

Calculate COD (mg/l or ppm) where N = Normality of FAS as determined by standardization.

$$\text{COD, mg/l} = \frac{(a - b) \times N \times 8000}{\text{ml original sample}}$$

CHEMICAL OXYGEN DEMAND (Low Level)

1. Scope and Application

   1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.

   1.2 This method (low level) is applicable for samples having a COD in the range of 5 - 50 mg/l COD.

2. Summary of Method

   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid in solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sampling and Preservation

   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

   3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

   3.3 Samples may be preserved with sulfuric acid at a rate of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

   4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103° C for two hours, in distilled water and dilute to 1000 ml. Mix this solution thoroughly then dilute 100.0 ml to 1000 ml with distilled water.

6.3 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.4 Standard ferrous ammonium sulfate (0.025 N): Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4 (6.8), cool and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against $K_2CR_2O_7$ solution.

6.4.1 Standardization: To 15 ml of distilled water add 10.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2) solution. Add 20 ml of H_2SO_4 (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 1 drop of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.5 Mercuric sulfate: Powdered $HgSO_4$

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1 - 10 (ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate: Powdered Ag_2SO_4

6.8 Sulfuric acid (sp. gr. 1.84): Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 1g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl until mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

7.2 With the reflux flask still in the ice bath, place 50.0 ml of sample or an aliquot diluted to 50.0 ml into the reflux flask.

CAUTION: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

7.3 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.4 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.5 Blank -- Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/liter} = \frac{(A-B)N \times 8000}{S}$$

Where

A = milliliters of $Fe(NH_4)_2 (SO_4)_2$ solution required for titration blank,

B = milliliters of $Fe(NH_4)_2 (SO_4)_2$ solution required for titration of the sample,

N = normality of the $Fe(NH_4)_2 (SO_4)_2$ solution and

S = milliliters of sample used for the test

9. Precision and Accuracy

9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 12.3 mg/l COD. The standard deviation was ± 4.15 mg/l COD with an accuracy as percent relative error (bias) of 0.3%. (EPA Method Research Study 3.)

DATE_____ BY_____

SAMPLE	_____	_____	_____
ML OF SAMPLE	_____	_____	_____
ML OF ACID REAGENT	_____	_____	_____
ML OF DICHROMATE	_____	_____	_____
START OF BOILING	_____	_____	_____
END OF BOILING	_____	_____	_____
ML OF F.A.S. USED	_____	_____	_____
C.O.D. MG/L	_____	_____	_____
SAMPLE	_____	_____	_____
ML OF SAMPLE	_____	_____	_____
ML OF ACID	_____	_____	_____
ML OF DICHROMATE	_____	_____	_____
START OF BOILING	_____	_____	_____
END OF BOILING	_____	_____	_____
ML OF F.A.S USED	_____	_____	_____
C.O.D. MG/L	_____	_____	_____
F.A.S. STANDARDIZATION			
ML OF DICHROMATE	_____	_____	
ML OF F.A.S	_____	_____	
NORMALITY OF F.A.S.	_____	_____	AVE._____

SAMPLE_____ AVE C.O.D._____

SAMPLE_____ AVE C.O.D._____

SAMPLE_____ AVE C.O.D._____

Module No:	Module Title: COD
	Submodule Title:
Approx. Time: 30 Min.	Topic: Relationship of COD to BOD

Objectives:

Upon completion of this topic the participant should be able to:

1. Predict BOD dilutions from COD results given an historical set of BOD and COD results for the sample.

Instructional Aids:

Overheads

Instructional Approach:

Discussion

References:

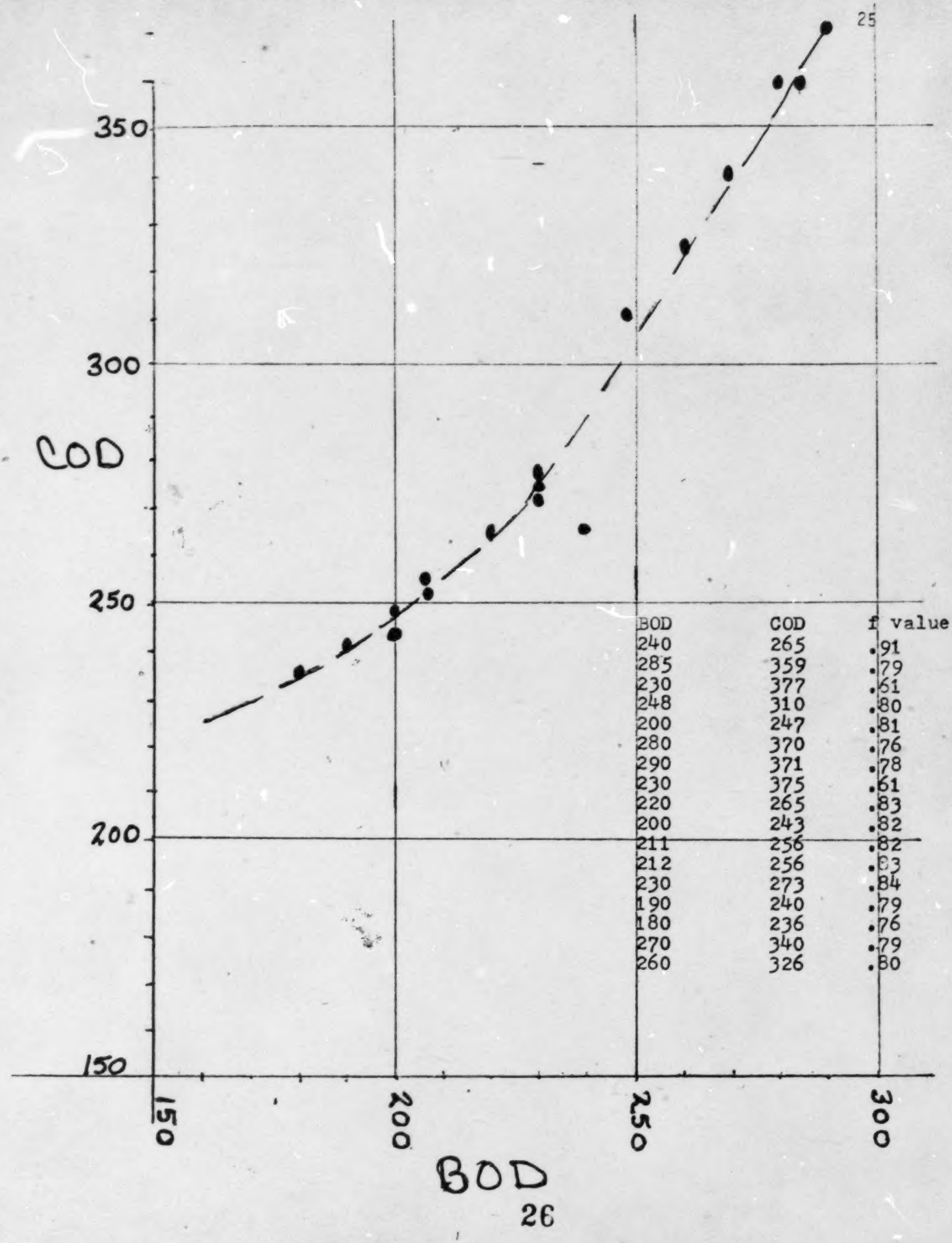
Sawyer and McCarthy, Chemistry for Sanitary Engineers

Class Assignments:

None

Module No:	Topic: Relationship of COD to BOD

Instructor Notes:	Instructor Outline:
Overhead Page 25 BOD - COD data	1. a. Discuss predicting BOD dilution factors from COD data. b. Work example problems. c. Show how to determine a correlation factor from a set of BOD - COD data.



BOD	COD	f value
240	265	.91
285	359	.79
230	377	.61
248	310	.80
200	247	.81
280	370	.76
290	371	.78
230	375	.61
220	265	.83
200	243	.82
211	256	.82
212	256	.83
230	273	.84
190	240	.79
180	236	.76
270	340	.79
260	326	.80

T F COD values are normally higher then BOD values.

T F The COD analysis is invalid if the color of the solution is green after digestion.

T F The titration of COD sample determines the amount of potassium dicromate left.

T F A blank COD analysis needs not be run.

T F A BOD value may be estimated from a COD value given a historical set of COD-BOD values for the sample.

T F FAS titrant need to be standardized weekly.

T F A COD sample may be preserved with acid and cooling for 7 days.